Observation of long photoluminescence decay times for high-quality GaN grown by metalorganic chemical vapor deposition

Ho Ki Kwon, C. J. Eiting,[a] D. J. H. Lambert, M. M. Wong, and R. D. Dupuis[b]
Microelectronics Research Center, The University of Texas at Austin, PRC/MER 1.606D-R9900, Austin, Texas 78712-1100

Z. Liliental-Weber and M. Benamara
Lawrence Berkely National Laboratory, One Cyclotron Road, Berkeley, California 94720

(Received 28 March 2000; accepted for publication 22 August 2000)

GaN epitaxial layers with different crystalline quality grown on sapphire substrates by metalorganic chemical vapor deposition are investigated using time-resolved photoluminescence at 300 K. It is found that the time-dependent photoluminescence of low-quality GaN decays faster than that of the high-quality GaN films. The time constants for the dual-exponential decay of the photoluminescence are calculated to be 50 and 250 ps for high-quality undoped GaN and 30 ps for low-quality undoped GaN. For high-quality Si-doped GaN, time constants of 150 and 740 ps are extracted while corresponding time constants of 40 and 200 ps are measured for low-quality Si-doped GaN. We believe that the time constant of 740 ps measured for our high-quality Si-doped GaN is the longest ever reported for thin GaN/sapphire films. © *2000 American Institute of Physics.* [S0003-6951(00)01942-2]

GaN and related materials have been extensively studied since the advent of high-brightness blue light emitting diodes.[1] Recently there have been many reports on the temporal characteristics of the optical properties of GaN epitaxial layers using time-resolved photoluminescence (TRPL).[2–8] TRPL is well known to be a powerful experimental tool to characterize excess carrier dynamics in semiconductors and to obtain basic constants such as the minority carrier lifetime and the surface recombination velocity. The carrier lifetime is a critical parameter in electronic devices, e.g., for the transport of electrons across the base in heterojunction bipolar transistors and for conductivity modulation in a *p-i-n* rectifier having a thick *i* region.

Most of these reports have focused on the TRPL characteristics of GaN measured at low temperatures (i.e., 2–10 K).[5–8] Since most optical devices are operated at room temperature, understanding the fundamental excess carrier recombination dynamics at 300 K is required to understand the relevant radiative and nonradiative recombination mechanisms and thus to improve the performance of optical devices. Furthermore the rapid progress in the improvement of the crystalline quality of GaN demands the reexamination of the values of the basics constants.

Most of the TRPL lifetimes measured for GaN/sapphire films at low temperatures are in the range of 35–340 ps for free and donor-bound excitons.[5–7] Several reports have shown that the TRPL lifetimes measured at higher temperatures for GaN grown by metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy decrease with increasing temperature.[5,6] There are only a few reports related to the TRPL lifetimes of excess carriers in GaN at 300 K. Im *et al.* reported a 300 K PL decay time of 38 ps for GaN grown by MOCVD.[2] The PL lifetime of free excitons in GaN at 295 K was reported to be 530 ps for an unintentionally doped 63 μm thick GaN film grown on sapphire by hydride vapor-phase epitaxy (HVPE).[4] In addition, Chichibu *et al.* reported a comparison of the TRPL lifetime of GaN/sapphire films grown using lateral epitaxial overgrowth (LEO). The TRPL exhibited a two-exponential decay with lifetimes of ~130 and ~400 ps that were observed both for the LEO ''window'' and the ''wing'' regions. However, long dual-exponential TRPL lifetimes of 130 and 860 ps were obtained for an 80 μm thick ''pure GaN substrate.''[3]

In this letter, we report the results of a TRPL study of GaN/sapphire heteroepitaxial layers grown by MOCVD having different crystalline quality. It is found that the low quality (LQ) GaN has shorter TRPL decay time than the high quality (HQ) GaN. These results are consistent with time-resolved reflectivity measurements.[9] Furthermore, the 300 K PL decay time of HQ Si-doped GaN is found to be the longest ever reported for GaN thin films.

Undoped and Si-doped GaN films were grown on (0001) Al_2O_3 by low-pressure MOCVD using an EMCORE D125 UTM reactor. Hydrogen was used as the carrier gas and trimethylgallium and NH_3 were used as precursors. The films were grown on (0001) Al_2O_3 substrates using a thin (~30 nm) low-temperature GaN buffer layer and a high-temperature GaN layer grown at 1050 °C at a reactor pressure of ~200 Torr. By optimizing the GaN growth conditions, we can grow GaN films having a reduced dislocation density. Details of the growth conditions will be reported later. The surface morphology of the GaN layers were characterized by atomic force microscopy (AFM) using a Digital Instruments Dimension 3000 AFM operating in tapping mode. For PL and TRPL measurements, the output of tunable Ti:sapphire laser with a pulse duration of 200 fs was frequency-tripled to $\lambda \sim 310$ nm by using nonlinear crystals.

[a]Present address: Air Force Research Laboratory, Wright-Patterson AFB OH 45433-7707.
[b]Author to whom correspondence should be addressed; electronic mail: dupuis@mail.utexas.edu

TABLE I. X-ray FWHM, dislocation density, rms surface roughness, and TRPL decay time for undoped and Si-doped GaN with different crystalline quality (LQ: low quality, HQ: high quality).

Sample description	(10–12) FWHM (arc sec)	(0002) FWHM (arc sec)	Dislocation density (cm^{-2})	rms surface roughness (nm)	TRPL decay time (ps)
LQ GaN:ud	1067	425	2×10^9	0.28	30
HQ GaN:ud	562	338	4×10^8	0.26	50, 250
LQ GaN:Si	770	352	1×10^9	0.23	40, 200
HQ GaN:Si	427	264	2×10^8	0.27	150, 740

The average output power of the laser was ~140 μW. A time-correlated single-photon counting detection system was used to measure the TRPL spectra with a microchannel-plate photomultiplier. The decay times of the TRPL spectra were calculated by fitting the data with an exponential time-decay model and numerical deconvolution techniques.

Table I displays a summary of the measurement results of the samples in this study using x-ray and AFM measurements to evaluate crystalline quality. The decrease of the x-ray full width half maximum (FWHM) and the dislocation density is clearly indicated in the data for the HQ GaN. In undoped GaN, the LQ GaN has an (10–12) x-ray FWHM of 1067 arc sec, and (0002) x-ray FWHM of 425 arc sec, and a measured (using AFM) dislocation density of $2\times10^9\,cm^{-2}$. The corresponding numbers for the HQ GaN are 562 arc sec, 338 arc sec, and $4\times10^8\,cm^{-2}$ for (10–12), (0002) x-ray FWHM and dislocation density, respectively. This improvement of the x-ray FWHM and dislocation density indicates an improvement of the crystalline quality. This result is also confirmed by plan-view and cross-section transmission electron microscope analysis.[10] We have found that the (10–12) x-ray FWHM decreases much more than the (0002) x-ray FWHM as the dislocation density drops in HQ undoped GaN. Heying *et al.* reported that the x-ray rocking curve on off-axis planes, such as (10–12), was a more reliable indicator of structural quality than that on on-axis planes such as (0002) because it reflected the effect of the threading dislocations in the film more efficiently.[11] Our experimental results are consistent with their results. This trend is also the same for Si-doped GaN. The HQ (LQ) Si-doped GaN has a (10–12) x-ray FWHM of 427 (770) arc sec, a (0002) x-ray FWHM of 264 (352) arc sec, and a dislocation density of 2×10^8 $(1\times10^9)cm^{-2}$, respectively. However, the root-mean-square (rms) surface roughness values measured by AFM are nearly the same value of about 0.25 nm for both LQ and HQ GaN.

Figure 1 shows the PL spectra measured at room temperature for undoped and Si-doped GaN. In Fig. 1(a), the free exciton was observed at 3606 Å (3.4359 eV) and 3603 Å (3.4388 eV) for LQ and HQ undoped GaN, respectively. The difference in the peak energy can be attributed to the different residual strains. The PL intensity of HQ undoped GaN is more than three times higher than that of LQ undoped GaN. The free exciton in Si-doped GaN was observed at 3612 Å (3.4302 eV) and 3608 Å (3.4340 eV) for LQ and HQ GaN, respectively. The PL intensity of HQ Si-doped GaN is larger by a factor of 5 than that of LQ Si-doped GaN. Although the yellow luminescence is observed in Si-doped GaN, the PL intensity of the free exciton in HQ Si-doped GaN is higher by an order of magnitude than that in LQ undoped GaN. Furthermore, the PL intensity of the HQ undoped GaN was larger than that of LQ Si-doped GaN. This is consistent with the fact that the crystalline quality of HQ undoped GaN is better than that in LQ Si-doped GaN.

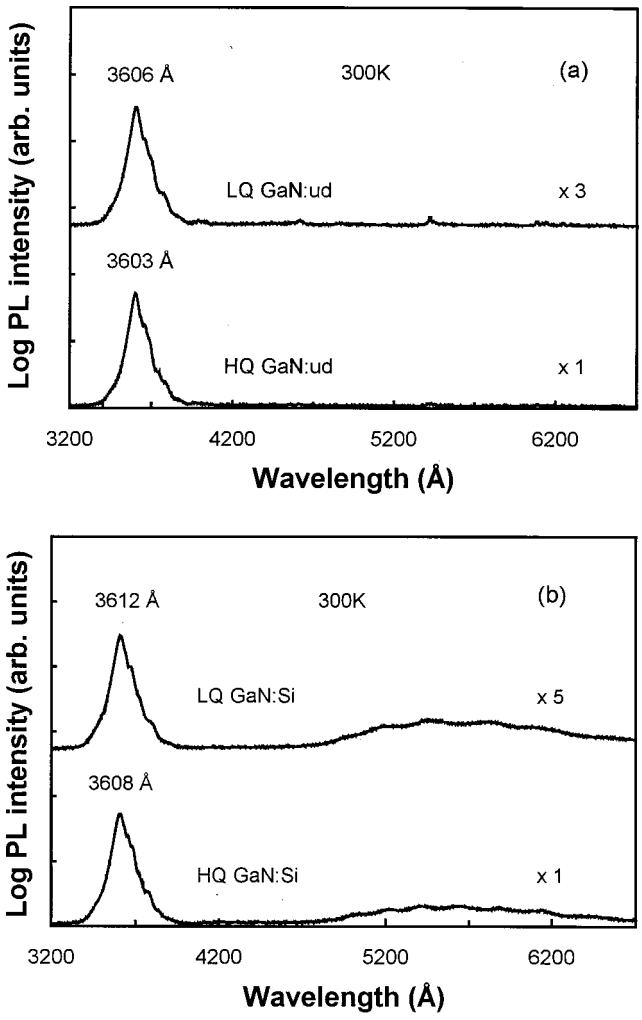

FIG. 1. PL spectra for (a) undoped and (b) Si-doped GaN at 300 K. The PL intensity of HQ undoped (Si-doped) GaN is larger by a factor of 3 (5) than that of LQ undoped (Si-doped) GaN.

The TRPL spectra of undoped and Si-doped GaN at room temperature are shown in Fig. 2. For LQ undoped GaN, the PL intensity decays fast, within 1.5 ns, and can be fitted with a single exponential function $[I(t)=A_1\exp(-t/\tau_1)]$ with the time constant of $\tau_1=30$ ps. This value is comparable to the luminescence decay time of 38 ps reported previously for GaN/sapphire grown by low-pressure MOCVD.[2] The PL decay time for HQ undoped GaN is measured to be longer than that of LQ undoped GaN. The TRPL data require two exponential functions $[I(t)=A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)]$ for a perfect fit and the time constants are calculated to be $\tau_1=50$ and $\tau_2=250$ ps. It is notable that the decay time for the HQ undoped GaN is longer than that for the LQ undoped GaN. The decay times of the LQ Si-doped GaN are 40 and 200 ps, which is longer than that of the LQ undoped GaN. However, the decay time for the HQ undoped GaN (250 ps) is longer than that for the LQ Si-doped GaN (200 ps). This is also consistent with the relative crystalline quality, as measured by x-ray and AFM (see Table I). The

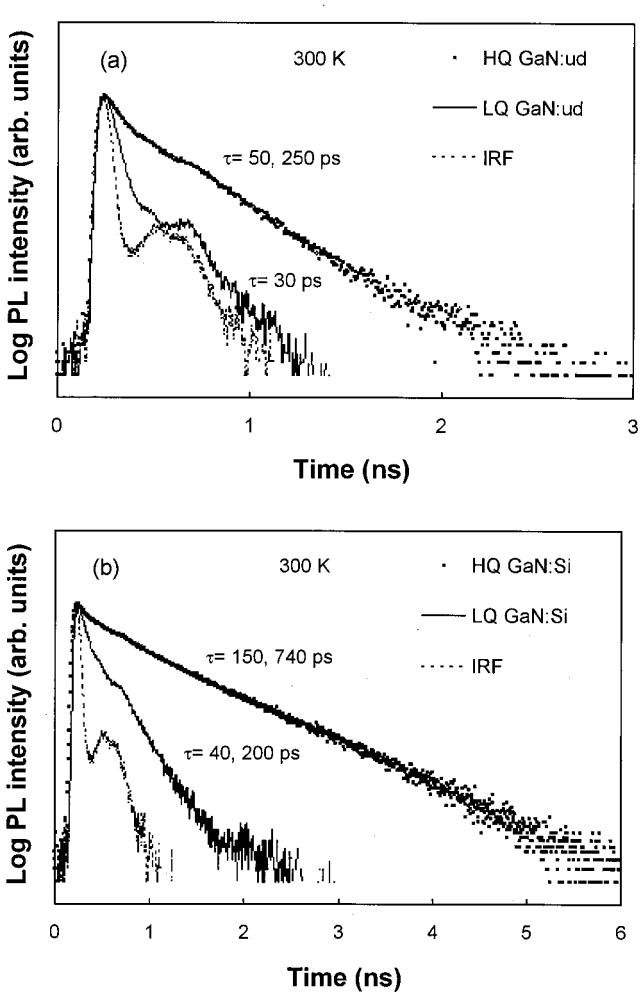

FIG. 2. TRPL spectra for (a) undoped and (b) Si-doped GaN at 300 K. The dotted line shows the instrument response function (IRF). The solid line and the circles indicate the PL decay curve for LQ and HQ GaN, respectively. We note that the decay time for HQ GaN is longer than that of LQ GaN.

PL decay times for HQ Si-doped GaN are measured to be 150 and 740 ps using two exponential functions. It should be noted that the decay time of 740 ps measured for the free exciton is the longest ever reported in GaN thin films. This value is also longer than the decay time of 530 ps measured for a 63 μm thick HVPE GaN film[4] and comparable to the result reported for the 80 μm thick GaN substrate (i.e., 130 and 800 ps).[3] We note that these TRPL data are similar to those we have obtained on other HQ and LQ GaN/sapphire samples with similar structural characteristics. A study on the temperature and excitation dependence of the TRPL characteristics of these GaN films is underway.

In summary, we have used time-correlated single-photon counting TRPL measurements at room temperature to study the free exciton recombination of excess carriers in undoped and Si-doped GaN/sapphire films grown by MOCVD. The (10–12) x-ray FWHM and dislocation density is 562 arc sec and $4\times10^8\,\mathrm{cm}^{-2}$ in HQ undoped GaN, and 427 arc sec and $2\times10^8\,\mathrm{cm}^{-2}$ in HQ Si-doped GaN, respectively. The HQ GaN layers have a larger 300 K PL intensity than the LQ GaN layers. The PL intensity in HQ Si-doped GaN is higher by an order of magnitude than that in LQ undoped GaN. The decay time is also observed to be longer in HQ GaN than in LQ GaN. We note that the TRPL decay times measured for our HQ Si-doped GaN are 150 and 740 ps, which are the longest ever reported for a GaN thin film at 300 K and are comparable to the results of 130 and 800 ps obtained for a 80 μm thick GaN substrate.

The authors thank the Division of Materials Research of the National Science Foundation, the Office of Naval Research (John Zolper), and DARPA (Robert Leheny) for support of this work.

[1] S. Nakamura, T. Mukai, and M. Senoh, Appl. Phys. Lett. **64**, 1687 (1994).
[2] J. S. Im, A. Moritz, F. Steuber, V. Härle, and A. Hangleiter, Appl. Phys. Lett. **70**, 631 (1997).
[3] S. F. Chichibu, H. Marchand, M. S. Minsky, S. Keller, P. T. Fini, J. P. Ibbetson, S. B. Fleischer, J. S. Speck, J. E. Bowers, E. Hu, U. K. Mishra, S. P. DenBaars, T. Deguchi, T. Sota, and S. Nakamura, Appl. Phys. Lett. **74**, 1460 (1999).
[4] G. E. Bunea, W. D. Herzog, M. S. Ünlü, B. B. Goldberg, and R. J. Molnar, Appl. Phys. Lett. **75**, 838 (1999).
[5] G. D. Chen, M. Smith, J. Y. Lin, H. X. Jiang, M. A. Khan, and C. J. Sun, Appl. Phys. Lett. **67**, 1653 (1995).
[6] M. Smith, G. D. Chen, J. Z. Li, H. X. Jiang, A. Salvador, W. K. Kim, O. Aktas, A. Botchkarev, and H. Morkoç, Appl. Phys. Lett. **67**, 3387 (1995).
[7] W. Shan, X. C. Xie, J. J. Song, and B. Goldenberg, Appl. Phys. Lett. **67**, 2512 (1995).
[8] K. C. Zeng, J. Y. Lin, H. X. Jiang, and W. Yang, Appl. Phys. Lett. **74**, 3821 (1999).
[9] M. Wraback, H. Shen, C. J. Eiting, J. C. Carrano, and R. D. Dupuis, Proceedings of the Fall 1999 MRS Symposium (to be published).
[10] Z. Liliental-Weber, M. Benamara, D. J. H. Lambert, M. M. Wong, U. Chowdhury, H. K. Kwon, and R. D. Dupuis (unpublished data).
[11] B. Heying, X. H. Wu, S. Keller, Y. Li, D. Kapolnek, B. P. Keller, S. P. DenBaars, and J. S. Speck, Appl. Phys. Lett. **68**, 643 (1996).